



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Suspension Polymerisation Process

We, "SHELL" RESEARCH LIMITED, a British company, of St. Helen's Court, Great St. Helen's, London, E.C.3., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the polymerisation of an ethylenically unsaturated organic compound which is conducted in an aqueous suspension.

The radical-addition polymerisation of an ethylenically unsaturated organic compound is often conducted in a suspension or dispersion of the monomer in water. The resulting polymer is produced in the form of beads, that is as small particles of solid polymer, which are suspended in the aqueous dispersion, such processes are therefore sometimes termed "bead", suspension or dispersion polymerisations. When such a polymerisation process is complete the polymer obtained may be readily separated from the dispersion by filtering or centrifuging the formed polymer beads from the aqueous medium and these beads are then readily purified by a simple washing procedure. If desired, the polymer particles may subsequently be further purified by an extrusion process in which the polymer is melted, forced through an extrusion die-head where it solidifies and then cut into small polymer particles called "nibs" which are very suitably used in moulding procedures and similar processing techniques.

The advantages of a suspension polymeri-

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sation process over one conducted in an emulsion or as a mass polymerisation process are that the resulting polymer is in a solid particulate form which particles are of high purity and can be readily separated from the reaction mixture and processed. Moreover in such a process the temperature is readily controlled and heat transfer problems are minimized. On the other hand an emulsion polymerisation has the disadvantage that a polymer latex is obtained which must first be coagulated to give a solid polymer before this can be separated from the surrounding medium, and a mass polymerisation process has the disadvantage that the resulting polymer is often found to contain an appreciable quantity of occluded monomer, which is only completely separated from the polymer with difficulty.

The disadvantage of operating a suspension polymerisation process is the difficulty of maintaining a satisfactory dispersion of the monomer or reaction medium in the aqueous medium that is preventing the agglomeration of the dispersed polymer beads formed during the polymerisation reaction, and of obtaining such beads in a suitable size. Although the monomer can be kept suspended in the aqueous medium by vigorous stirring or otherwise agitating the reaction mixture, this method does not give a stable suspension and it is necessary to use a suitable suspension stabiliser. Often this is a finely-divided solid which, when added to the reaction mixture, gives a stable suspension from which the solid does not settle out even if the mixture is only being

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stirred at a slow rate.

Various inorganic substances have been proposed as suspension stabilisers for use in the bead polymerisation of ethylenically unsaturated organic compounds. These include, for example, talc, clay, barium sulphate and calcium phosphate and oxalate. Water-soluble organic stabilisers have also been used in such polymerisation. For instance, polyvinyl alcohol has been found to give quite good results when used in a process for the suspension polymerisation of certain monomers, for example styrene; gelatine, fish-glue, pectin and salts of polyacrylic acids and styrene-maleic anhydride copolymers have also been proposed for this purpose, but the use of starch and gelatine as suspension stabilisers for the polymerisation of a solution of 6% by weight of a rubbery butadiene-styrene copolymer in monomeric styrene has been found to give poor results.

Therefore, as illustrated above in two particular instances, the suspension stabilisers of the prior art do not always give satisfactory results either in that the suspension obtained is not stable throughout the entire course of the polymerisation, or that polymer beads of an inconveniently small size are sometimes obtained. For the latter purpose it is desirable to obtain beads which are of uniform particle size and as large as possible, in so far as this is consistent with the greater purity normally obtained in beads of smaller size. There is a great variety of monomers which can be polymerised in a suspension process and the conditions for the polymerisation of each of such monomers vary to a great extent so that suspension stabiliser which is eminently satisfactory for the polymerisation of one monomer under certain conditions may be quite unsuitable for polymerising the same or a different monomer under different conditions or a different monomer under the same conditions. It has therefore been a matter for considerable research to find alternative suspension stabilisers to those of the prior art, which alternative stabilisers in special circumstances yield results which are comparable to or better than those obtained using the conventional stabilisers, for example those previously mentioned.

It has now been discovered that the polymerisation of an ethylenically unsaturated organic compound can be very suitably conducted in an aqueous suspension which is stabilised by the presence of a polyoxyalkylene oxide compound of high molecular weight. Such a polymerisation process proceeds smoothly and is readily amenable to good temperature control. Furthermore the polymers are often produced in a high state of purity and in beads of a very convenient size which may be quite substantial. Such

a use for polyalkylene oxide compounds is quite distinct from the well-known use of low molecular weight polyalkylene ether glycols and their derivatives as non-ionic emulsifying agents in polymerisation processes carried out in emulsion as distinct from suspension or bead polymerisation processes.

It has also been shown that such a polyalkylene oxide compound gives very advantageous results in a suspension polymerisation reaction when used in conjunction with a small amount of a surface-active agent, though the amount of surface-active agent used must not be so large that an emulsion polymerisation reaction would result. Furthermore it has been found that the presence of a small quantity of a water-soluble metal or ammonium halide in the aqueous medium in which a suspension polymerisation of the above-described kind is to be conducted results in a reduced particle size of the polymer beads being obtained; this reduced particle size is often desirable in the interests of obtaining beads of high purity.

Accordingly, the process of the present invention is one for the suspension polymerisation of a normally water-insoluble ethylenically unsaturated organic compound capable of radical-addition polymerisation by a suspension polymerisation process, which process comprises polymerising the organic compound in aqueous suspension in the presence as suspension stabiliser of a minor amount of a polyalkylene oxide compound as hereinafter defined having a molecular weight of at least 20,000 and, optionally, a surface-active agent, and/or a water-soluble metal or ammonium halide which is present in an amount not greater than 5% by weight based on the weight of water present.

The polyalkylene oxide compound for use in the process of the present invention is hereby defined as one that has been derived by polymerisation of an alkylene oxide or copolymerisation of a mixture of alkylene oxides. The term polyalkylene oxide compound is herein intended to extend not only to polyalkylene ether glycols but also to ethers and esters of such glycols. Thus, normally, the polyalkylene oxide compound used will be one of the general formula



where each X represents hydrogen or an alkyl, aryl, acyl or aroyl group, each R represents a divalent aliphatic or substituted aliphatic group other than a methylene or substituted methylene group and n is an integer sufficiently large to give the polyalkylene oxide compound a molecular weight of at least 20,000 (compounds of the above formula except that R is a methylene or substituted methylene group are more cor-

rectly designated as polyaldehydes or derivatives of polyformaldehyde and, as such, their use is outside the scope of the present invention). Furthermore, if desired, the polyalkylene oxide compound may be one which has been derived from a polyhydroxy nucleating agent by condensation of its hydroxyl groups with an alkylene oxide to produce a polyalkylene oxide compound of the desired molecular weight; for instance a condensation product of the formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_n\text{OH}$ which is derived from ethylene oxide and a dihydroxy benzene such as hydroquinone or resorcinol. It is of course possible to use as such a polyhydroxy nucleating agent a trihydroxy compound such as glycerol, pyrogallol, or a tetrahydroxy compound such as pentaerythritol.

Preferred polyalkylene oxide compounds for use in the present invention are those derived from the homo- or co-polymerisation of styrene oxide and lower alkylene oxides such as ethylene oxide; 1,2-propylene oxide; 1,3-propylene oxide; tetrahydrofuran; and 1,2-butylen oxide; that is compounds of the general formula $\text{XO}(\text{R}'\text{O})_n\text{X}$ where each X represents a hydrogen atom or an alkyl, aryl, acyl or aroyl group, each R' represents a divalent aliphatic group having 2 to 4 carbon atoms or an α -phenylethylene group and n is an integer sufficiently large to give the polyalkylene oxide compound a molecular weight of at least 20,000. The self- or inter-polymers of ethylene oxide and 1,2-propylene oxide are particularly useful in the process of the invention.

The polyalkylene oxide compounds for use in the present process have a minimum molecular weight of 20,000 and, as previously explained, they may be polymeric glycols or mono- or di-ethers or esters thereof. However, the preferred compounds are polyalkylene oxides, that is polyalkylene ether glycols, having a molecular weight of 200,000 to 3,000,000. Polyalkylene oxides, and particularly polyethylene oxides, having a molecular weight of the order of 400,000 are especially suitable for the present process. The limitation of the invention to the use of polyalkylene oxides having a molecular weight greater than 20,000 is an approximate one as the exact determination of the molecular weight of any particular sample of a polyalkylene oxide is not readily made. Furthermore any such molecular weight determination gives an average value which may vary to a small degree depending upon the molecular weight determination method used. However, the high molecular weight polyalkylene oxides used in the present invention constitute a readily recognisable class of compounds quite distinguishable from the polyalkylene oxide compounds, hitherto commercially available, that have

molecular weights of the order of not more than a few thousand. The molecular weights of such low molecular weight compounds are readily determined from measurements of their hydroxyl number, but the high molecular weight polyalkylene oxides have too low a hydroxyl number to enable an accurate determination of their molecular weight to be made by this method.

The molecular weight of the polyalkylene oxide used in the present invention may be determined by any of the conventional methods used for determination of the molecular weights of polymeric materials of high molecular weight, for example by osmometry or by viscometry. The molecular weight of a sample of a polyethylene oxide is readily determinable by measurement of the intrinsic viscosity at 35°C of a 0.1% solution of the compound in water and using the following conversion factor given in The Journal of Applied Polymer Science, Volume, no. 1, page 60, namely:

$$\text{IV} = 6.4 \times 10^{-5} \text{M}^{0.82}$$

where I.V. is the intrinsic viscosity of the polyethylene oxide at 35°C and M is its average molecular weight; the molecular weights of the various polyethylene oxides used in the following Examples have been determined by this method and by making use of the above relation between intrinsic viscosity and molecular weight.

Polyalkylene oxides of molecular weight above 20,000 may be prepared from the monomeric compounds in several different ways. For instance, alkylene oxides may be polymerised to produce these high molecular weight polymers in the presence of catalysts of various types, which include, among others, alkoxides and aroxides of metals from Groups 2 to 5 of the Periodic Table of elements; metal alkyls and metal alkyl halides derived from metals of Group 2 and 3 of the Periodic Table and Friedel-Crafts catalyst complexes such as complexes of the alkylene oxide with ferric or stannic chloride. It has also been proposed to use as catalysts for the polymerisation of alkylene oxides certain synergistic combinations of the catalysts described above. The mono- or di-ethers and esters of the polyalkylene oxides may be prepared from the polyalkylene oxides themselves, that is the polyalkylene ether glycols, in the conventional manner.

The polyalkylene oxide compounds which find use in the present invention are solid materials which have only a limited solubility in water. It is believed that some solubility of the polyalkylene oxide compound in water is desirable and accordingly a polyethylene oxide is the preferred suspension stabiliser of the invention, as such a compound has a greater solubility in water than a polypropylene or higher oxide.

The amount of polyalkylene oxide compound required to give a stable dispersion of the monomer in water depends upon the nature of the monomer and the conditions to which the dispersion is to be subjected. It is of course desirable to use the minimum amount of polyalkylene oxide compound necessary to give a stable suspension of the monomer in the aqueous medium as there is then less risk of contamination of the formed polymer by the excess suspending agent, that is the polyalkylene oxide compound, and polymer beads of larger size are also more likely to be obtained. An amount of polyalkylene oxide compound between 0.1 and 5%, and particularly between 0.3 and 1%, by weight based on the monomer has been found to be particularly suitable for the purposes of the invention. However, the optimum amount of polyalkylene oxide is in some ways dependent on its molecular weight and if this is not of the preferred order, it may be necessary to use a slightly higher proportion of the polyalkylene oxide. The minimum amount of polyalkylene oxide which gives completely satisfactory dispersion of the monomer or monomers in the aqueous medium throughout the course of the polymerisation and at the same time results in the ready production of beads of suitable purity and size can readily be found from the results of a few small scale tests. In most cases an amount of about 0.5% by weight of the monomer will be found to be eminently suitable, though in particularly favourable cases an amount of 0.3% may well suffice. If desired the polyalkylene oxide compounds can be used in conjunction with the suspension stabilisers of the prior art. Often, it may be desirable to use a small amount of a surface-active agent, that is to say an emulsifying agent for the monomer, in conjunction with the polyalkylene oxide compound as thereby the amount of polyalkylene oxide compound required may be reduced and good reproducible results are then normally obtained. However, the surface-active agent must not be present in an amount which would cause an emulsion polymerisation reaction to occur, that is to say the polymer product must still be obtained in the form of polymer beads and not in latex form as in the case of an emulsion polymerisation reaction. Thus normally the surface-active agent will not be present in an amount by weight greater than that of the polyalkylene oxide compound. Preferably an amount of surface-active agent of from 5 to 15% by weight of polyalkylene oxide compound is used in conjunction with the polyalkylene oxide compound present as suspension stabiliser and an amount of from 8 to 12% is especially useful. The surface-active agent may be an

anionic, cationic or non-ionic surface-active agent, but ionic, especially anionic, agents are preferred. Thus there can very conveniently be used an alkali metal salt of a long chain fatty carboxylic acid such as stearic, palmitic or oleic acid as well as rosin acid soaps and alkali metal salts of alkylaryl sulphonic acids and alkyl-sulphuric and -sulphonic acids; the alkali metal alkylaryl sulphonates, particularly the dodecylbenzene sulphonates, are especially useful in the process of the present invention. As cationic surface-active agents there may be used, for example, cetylpyridinium bromide and octadecylammonium chloride. Non-ionic surface-active agents may also be employed, for instance low molecular weight polyalkylene oxide compounds which have been mono-etherified with an alcohol or phenol, for example condensates of ethylene oxide and cetyl alcohol or octyl phenol, or mono-esterified with a carboxylic acid such as oleic acid. Mixtures of two or more surface-active agents can be used if desired.

The monomer to be polymerised is one which is normally insoluble in water and capable of radical-addition polymerisation by a suspension polymerisation process. Thus the process of the invention finds particular application in the suspension polymerisation of styrene and vinyl chloride. However, the process may also be used to polymerise vinyl-aromatic compounds in general, that is to polymerise, for example, vinyl toluene, divinyl benzene, α -methyl styrene and nuclear halogenated styrenes, as well as mixtures of one or more of such vinyl aromatic compounds including styrene with one or more conjugated dienes such as butadiene, isoprene, chloroprene, 2,3-dimethyl-butadiene and piperylene to form resinous copolymers. Ethylenically unsaturated organic compounds which are not hydrocarbons may also be polymerised by the process of the invention. Thus, for instance, besides vinyl chloride which is particularly suitably polymerised by the present process, there may be polymerised vinylidene chloride, acrylonitrile and the lower alkyl esters of acrylic and methacrylic acids, that is those in which the alkyl group contains not more than four carbon atoms, for example methyl methacrylate and ethyl acrylate. Mixtures of two or more ethylenically unsaturated organic compounds may of course be copolymerised and the process of the invention is particularly suited to the production of graft copolymers by the polymerisation of one or more monomers in the presence of a preformed polymer or copolymer. For instance, there may be produced by the process of the invention a modified or toughened polystyrene having a high impact strength by polymerising styrene in the presence of a

preformed sulphur-vulcanisable rubbery polymer such as, for example, polybutadiene, polyisoprene, a rubbery butadiene-styrene or butadiene-acrylonitrile copolymer or in the presence of a natural rubber material. Such preformed polymers can of course have been previously prepared by any suitable polymerisation process and, if desired, the preformed polymers can comprise the stereo-specific polydienes such as cis-1,4-isoprene or cis- or trans-1,4-polybutadiene or the elastomeric ethylene-propylene copolymers.

If desired, the monomer or monomers can be subjected to a pre-polymerisation step carried out as a mass polymerisation and then the partially polymerised pre-polymer produced is suspended in an aqueous medium using one of the specified polyalkylene oxide compounds as the suspension stabiliser, if desired in the presence of a surface-active agent, and the polymerisation completed by the process of the invention. If desired, in such a process a further quantity of monomer can be added to the dispersion during a modified polystyrene material of high impact strength may be very advantageously obtained by subjecting a solution of a rubbery styrene-butadiene copolymer in monomeric styrene to a pre-polymerisation stage by heating the mixture in the absence of water, if necessary in the presence of a peroxide initiator, until approximately 15% by weight of the monomeric styrene has polymerised. The mixture is then dispersed in approximately an equal volume of water, the polyalkylene oxide added as suspension stabiliser and the dispersion then agitated and subjected to polymerising conditions. There are obtained beads of a high-impact polystyrene which are readily separated by centrifuging the reaction mixture.

In the preferred embodiment of the invention, as outlined immediately above, there may conveniently be used a pre-polymerisation stage which is sufficient to polymerise from 5 to 40%, particularly from 10 to 25% and especially from 15 to 20% by weight of the monomer. Such a pre-polymerisation stage is carried out in the absence of water, but there may be present conventional additives such as radical-addition polymerisation initiators; for example, peroxy compounds such as benzoyl or lauryl peroxide, tert.-butyl perbenzoate, cumyl hydroperoxide, or azo compounds such as azo-bis-isobutyronitrile or azo-bis-cyclohexane carbonitrile; chain transfer agents, for example tert.-dodecyl mercaptan; lubricants such as butyl stearate and glycerol mono-stearate, and other additives such as, for example, antioxidants and fillers. The pre-polymerisation stage can, if desired, be carried out in the absence of a radical-addition initiator, the polymerisa-

tion being initiated by ionizing radiation, ultra-violet light or simply by heating the reaction mixture to a suitable temperature.

When the preferred embodiment of the invention is used to prepare a high impact polystyrene it is convenient to dissolve a proportion, usually between 3 and 40% and particularly between 5 and 10%, of a rubbery polymer in the monomeric styrene, to subject this solution to a pre-polymerisation step and then to disperse the pre-polymerised mass in water with the aid of the polyalkylene oxide suspension stabiliser before completing the polymerisation reaction as a suspension process. The rubber is very suitably a styrene-butadiene copolymer of the GR-S type, that is one prepared from 60-90% by weight of butadiene and 40 to 10% of styrene, though there may also be used rubbery butadiene-acrylonitrile copolymers, polybutadiene, polyisoprene or natural rubber, as well as the stereospecific polymers such as cis-1,4-polyisoprene, cis- or trans-1,4-polybutadiene or an elastomeric ethylene-propylene copolymer. If necessary the rubber may contain a small amount of an antioxidant or other antidegradant.

When a pre-polymerisation stage is used, the mass polymerisation is interrupted after a suitable polymerisation time and the partially polymerised mass then dispersed in an aqueous medium. This is usually water, but if desired it can be an aqueous solution of a suitable salt. Normally it is desirable to disperse the pre-polymerised mass in the ratio of 1 part of pre-polymer to between 0.5 and 5 parts by volume of water, though smaller or larger ratios can be used; particularly good results are achieved when the pre-polymerised mass is dispersed in approximately an equal volume of water. When no pre-polymerisation stage is used it will be found very suitable to disperse the monomer in from 1 to 5 parts by weight of water. Thus when vinyl chloride is polymerised by the process of the invention it is very convenient to disperse the monomer in about 2.5 parts by weight of water.

The suspension process of the invention is normally carried out in the presence of a radical-addition polymerisation initiator such as an organic peroxide or hydroperoxide or an aliphatic or cyclo-aliphatic azo compound. It is usual to stir the reaction mixture during the polymerisation process, which is preferably conducted in an inert atmosphere, for example under nitrogen or hydrogen, in order to avoid the deleterious effects which may result when radical-addition polymerisations are conducted in the presence of air or oxygen. It is therefore desirable to purge the suspension before subjecting it to polymerising conditions with a stream of an inert gas, such as nitrogen. If desired, there may be incorporated in the

suspension other materials such as chain-transfer agents, for example, tert-dodecyl mercaptan, lubricants such as, for example, stearic acid or butyl stearate and anti-oxidants such as, for example, 2-tert-butyl-4-methyl phenol, styreneated resorcinol, tris-(nonyl-phenyl) phosphite and N-substituted phenylene diamines.

The process of the invention may be conducted at the usual temperature for suspension polymerisation processes. Often this will be between 50 °C and 100 °C, though higher or lower temperatures can be employed where necessary. When temperatures which are in excess of the boiling point of the monomer are employed it will be necessary to conduct the polymerisation in a pressurized reactor to prevent loss of the monomer by evaporation. It is then highly desirable to pressurize the reactor with an inert gas such as nitrogen in order to prevent the polymerisation reaction from being affected by the presence of oxygen in the reaction system. Alternatively, the monomer may be suitably polymerised in a closed reactor under autogenic pressure at a suitable temperature, for example, vinyl chloride may be so polymerised at a temperature of approximately 50 °C, and styrene at a temperature up to about 130 °C, though in this case it is usual to commence the polymerisation at a temperature below 100 °C and raise it to a figure above 100 °C only in the later stages of the reaction.

The aqueous suspension in which the process of the invention is conducted should, preferably, have a controlled pH as variations in the acidity and alkalinity of the reaction mixture often have a considerable effect on the rate of polymerisation and the effectiveness of the suspension stabiliser. Furthermore, it is found that the polyalkylene oxide compound used as suspension stabiliser tends to be unstable in an acidic medium. Thus it is desirable that the reaction mixture should be maintained within a pH of 7 to 11. It is particularly found that control of pH becomes more important as the amount of polyalkylene oxide compound is decreased and, if desired, control of pH may in many cases be obviated by the use of larger quantities of the stabiliser, though if possible an excess of the polyalkylene oxide compound is desirably avoided, as previously explained. The alkalinity of the reaction mixture can be suitably maintained by the addition of a buffer compound; for example small quantities of sodium borate or sodium acetate or even sodium hydroxide can be added to the reaction mixture and the pH of the mixture thereby controlled and maintained at a convenient value.

In addition to the desirability of controlling the pH of the reaction medium, it

has been found that the size of the polymer particles produced can often be considerably reduced if there is present in the aqueous reaction medium up to 5% by weight based on the weight of water present of a water-soluble metal or ammonium halide. Preferably such a halide is a chloride and the use of potassium and sodium chlorides has been shown to give good results. Normally the amount of such halides used will be less than 1% by weight based on the weight of water present and an amount of from 0.4 to 0.7% has been found to be especially useful. This reduction in the particle size of the polymer beads may sometimes be very desirable in order to produce beads containing very low quantities of impurity.

It may also be desirable in certain instances to add to the reaction mixture a small quantity of a sequestering agent, such as for example ethylene diamine tetraacetic acid or an N-hydroxymethyl ethylene diamine acetic acid, as in this way it may be possible to avoid undesirable effects arising from the presence of contaminants introduced into the system with the other constituents.

The suspension process of the invention results in the production of polymer beads. The beads produced by the invention are often of quite a large size and bead diameters of 0.05 to 0.07 inches are frequently obtained. The polymer beads are conveniently separated from the reaction mixture by filtration or by centrifuging the mixture and the separated beads are then washed well with water and dried. If desired, the polymer beads may be further purified by an extrusion process, the extruded material being chopped into small particles termed "nibs" which are very suitably used in conventional moulding and fabricating procedures.

The invention will now be illustrated by the following Examples.

EXAMPLE 1

In 100 parts by weight of monomeric styrene, which had been distilled in order to remove any dissolved polymerisation inhibitor, there was dissolved 6 parts by weight of a GR-S rubber crumb which had been prepared by the copolymerisation of 76.5% by weight of butadiene and 23.5% by weight of styrene at a temperature of about 50 °C and which contained about 1 part by weight of tris-(nonyl-phenyl) phosphite as rubber antioxidant. To this solution there was also added 3.5 parts by weight of butyl stearate as lubricant and the mixture was then purged with nitrogen to remove oxygen from the solution and thereafter pre-polymerised with stirring to a polymer conversion of monomeric styrene of about 15% by heating the mixture in bulk in the absence of a radical-addition polymerisation

initiator to a temperature of 105 °C for 4.75 hours.

The pre-polymerised mass was suspended in 150 parts by weight of water and the resulting suspension stabilised by the addition of 0.5% by weight of a polyethylene oxide having a molecular weight of approximately 400,000. To the mixture there was added 2 parts by weight of azo-bis-cyclohexane carbonitrile as radical-addition polymerisation initiator. The suspension was then purged with a stream of nitrogen and gently agitated whilst it was subjected to the following polymerisation cycle:

- 15 7 hours at 90 °C
- 1 hour at 100 °C
- 13 hours at 120 °C

Initially the polymerisation was conducted at atmospheric pressure but during the cycle it became necessary to conduct the reaction in a closed reactor under autogeneous pressure to prevent evaporation of monomer and water. At the end of the cycle it was found that a polymerisation conversion of 99.8% had occurred. The polymer beads obtained were separated from the reaction mixture, washed well with water and dried to yield a polystyrene having an impact strength of 1.04 foot pounds per Izod notch.

30 EXAMPLE 2

A solution of 6 parts by weight of the GR-S rubber in 100 parts by weight of monomeric styrene containing 3.5 parts by weight of butyl stearate was prepared as described in Example 1. This mixture was purged with nitrogen and then subjected to a bulk pre-polymerisation stage by heating it with stirring for 10 hours at 95 °C in the absence of a radical-addition polymerisation initiator; at the end of this time it was shown that approximately 15% by weight of the styrene had polymerised.

The pre-polymerised mass was suspended in 150 parts by weight of water containing 45 1 part by weight of a polyethylene oxide of molecular weight about 400,000 and the resulting dispersion purged with a stream of nitrogen and vigorously agitated. Polymerisation of the styrene was effected by adding to the mixture 0.2% by weight based on the styrene of benzoyl peroxide as polymerisation initiator and then subjecting the reaction mixture to a temperature of 92 °C for 24 hours, after which the polymer beads obtained were separated from the reaction mixture, washed well with water and dried. The polystyrene beads were found to be of a fairly large size having a diameter of 0.05 to 0.07 inches and were of high purity.

60 EXAMPLE 3

The process of Example 2 was repeated but using only 0.3 part by weight of the polyethylene oxide as suspension stabiliser. The polymerisation process proceeded perfectly satisfactorily. The polystyrene beads

obtained were of a conveniently large size and, moreover, were readily separated from the reaction mixture and purified.

EXAMPLE 4

Monomeric styrene which had been distilled to remove any polymerisation inhibitor was suspended in 5 times its volume of water using 1% by weight based on the styrene of a polyethylene oxide having a molecular weight of 1,800,000 as suspension stabiliser. There was then added to the suspension 0.2% by weight based on the styrene of benzoyl peroxide as polymerisation initiator and the polymerisation was conducted at 92 °C for 20 hours; the mixture being vigorously agitated throughout. After 2.5 hours of the polymerisation a further 0.2% of benzoyl peroxide was added to the reaction mixture. The polymerisation reaction proceeded smoothly throughout and polystyrene beads of good quality were obtained.

EXAMPLE 5

The procedure used to prepare the pre-polymer of Example 1 was repeated. The pre-polymerised mass was then dispersed in 5 times its own volume of water using 1% by weight based on the styrene of a polyethylene oxide of M.W. 400,000 as suspension stabiliser. To the suspension of monomer in water there was added 0.1% by weight based on the styrene of azo-bis-isobutyronitrile as polymerisation initiator and the polymerisation reaction was conducted at 92 °C for 10 hours; a further 0.1% of the initiator being added after 3 hours.

The polymerisation process proceeded smoothly and beads of a high impact polystyrene were obtained which were of good quality.

EXAMPLE 6

The procedure of Example 5 was repeated except that the mass pre-polymerisation stage was continued until 17.3% conversion had occurred and except that the initiators used were 0.2% by weight based on the styrene of tert-butyl perbenzoate added to the initial suspension of the pre-polymer and 0.2% by weight based on the styrene of benzoyl peroxide which was added after a further 3 hours.

The polymerisation proceeded smoothly and high impact polystyrene beads of good quality were obtained.

EXAMPLE 7

This Example illustrates the production of a high impact polystyrene on a larger scale than that used in the previous Examples.

A solution of 6% by weight of the GR-S rubber used in Example 1 was prepared in 0.4 gallons of monomeric styrene which had been distilled to remove polymerisation inhibitor. The solution was purged with

nitrogen to remove oxygen, agitated and heated for 6 hours under autogeneous pressure at 100 °C. The conversion in this mass pre-polymerisation stage was shown to be about 15%.

The pre-polymer and residual monomer were then dispersed in 0.6 gallon of water using 0.3% by weight based on the styrene of a polyethylene oxide of molecular weight 400,000. The pH of the suspension was adjusted to pH 10 to 11 by addition of a small quantity of aqueous sodium hydroxide solution. The dispersion was agitated and 0.2% by weight based on the styrene of azo-bis-isobutyronitrile and 0.05% by weight based on the styrene of tert.-butyl perbenzoate were added as polymerisation initiators. Agitation of the dispersion was continued while it was subjected to the following polymerisation cycle:—

2 hours at 68 °C
2 hours at 83 °C
2 hours at 115 °C
2 hours at 130 °C

At the end of this cycle the formed polymer beads were separated from the reaction mixture and were found to be well-formed and of comparatively large size. The impact strength of the material as shown to be 1.06 foot pound per Izod notch.

EXAMPLE 8

The procedure of Example 7 was repeated on a larger scale using 20 gallons of monomeric styrene and 30 gallons of water as dispersing medium for the pre-polymer obtained therefrom. There were formed at the end of the polymerisation cycle beads of similar good size and appearance as those which were produced in Example 7.

EXAMPLE 9

This Example illustrates the relationship between the molecular weight of the polyethylene oxide used as suspension stabiliser and the amount of it required to give the most satisfactory results in the production of beads of high impact polystyrene.

A solution in distilled monomeric styrene was prepared containing 3.5% by weight of butyl stearate as lubricant and 6% of a GR-S rubber which had been produced by copolymerisation of 76.5% by weight of butadiene and 23.5% by weight of styrene at a temperature of about 50 °C and which contained about 1% by weight of tris-(nonyl-phenyl) phosphite as antioxidant. The solution was purged with nitrogen to remove oxygen from the solution and thereafter polymerised with stirring to a polymer conversion of monomeric styrene of approximately 15% by heating the mixture in bulk in the absence of a polymerisation initiator to a temperature of 100 °C for 6 hours.

Samples of the pre-polymer were dispersed in 1.5 times their volume of water using a polyethylene oxide, of a molecular weight

and in a percentage by weight based on the weight of styrene as stated in Table I below. In each instance the dispersion was buffered at pH 9 by the addition of a boric acid/sodium hydroxide/potassium chloride aqueous solution as buffer and 0.2% by weight of benzoyl peroxide was added as polymerisation initiator. Each reaction mixture was then heated at 92 °C for approximately 20 hours.

The following Table describes the results of the polymerization reaction and the nature of the polymer beads obtained.

TABLE I

Molecular weight	Amount used %	Result
400,000	0.3	Dispersion satisfactory, good beads obtained.
400,000	0.2	Dispersion satisfactory, fairly good beads obtained.
100,000	0.15	Initial dispersion satisfactory, giving beads of fair quality, but dispersion not maintained throughout the polymerisation.
100,000	0.4	Initial dispersion and polymerisation satisfactory, but dispersion not maintained towards the completion of the polymerisation.
100,000	1.0	Dispersion satisfactory and beads of suitable size obtained, but difficulty experienced in maintaining complete dispersion towards the completion of the polymerisation.
100,000	2.5	Dispersion satisfactorily maintained throughout the polymerisation. Beads of good size and appearance obtained.
4,000,000	0.5	Dispersion obtained but this had a tendency to froth and form an aqueous emulsion of the monomer. Polymerisation satisfactory, polymer beads obtained.
4,000,000	0.2	Initial dispersion satisfactory, but polymer beads obtained were of only poor quality.
4,000,000	0.1	Initial dispersion difficult, poor polymer beads obtained.

This Example illustrates that preferably the polyethylene oxide used as a molecular weight in the region of 400,000 and that the quantity of the suspension stabiliser

required to achieve a completely satisfactory process with stabilisers of different molecular weights increases as the molecular weight varies from the preferred value of about 400,000.

EXAMPLE 10

This Example illustrates the suspension polymerisation of methyl methacrylate using a polyethylene oxide of high molecular weight as suspension stabiliser.

A dispersion of 80 grams of methyl methacrylate in 320 cc. of water was prepared using 1% of a polyethylene oxide of molecular weight approximately 400,000 as suspension stabiliser. There was also incorporated into the dispersion 0.2% by weight based on the methyl methacrylate of benzoyl peroxide as polymerisation initiator and the dispersion was purged with nitrogen to remove dissolved oxygen and heated under autogeneous pressure at 85 °C for 3.5 hours.

The polymerisation proceeded smoothly and beads of small size were obtained indicating that a smaller amount of the polyethylene oxide could probably have been used with advantage. However, the beads obtained were of good quality, and were readily separated from the reaction medium, washed and dried. The dried beads were compression moulded to give a disc of great clarity, thereby indicating that the beads obtained were of a satisfactory purity.

EXAMPLE 11

This Example illustrates the effect of using a small amount of a surface-active agent in conjunction with a polyalkylene oxide compound as suspension stabiliser in the production of a high impact polystyrene.

Eight exemplifying experiments (A to H) were each carried out as follows.

In 150 parts by weight of water there was suspended 100 parts by weight of a styrene pre-polymer containing 6% by weight of a butadiene-styrene copolymer and prepared by the method described in Example 9, the suspension being stabilised by the presence of a small percentage by weight (as specified in Table II below), based on the styrene, of a polyethylene oxide having a molecular weight of approximately 400,000 and also a small percentage by weight (as specified in Table II) based on the styrene of sodium dodecylbenzene sulphonate as anionic surface-active agent. To the mixture there was also added 0.3% by weight based on the pre-polymer of azo-bis-isobutyronitrile and 0.05% by weight based on the pre-polymer of tert-butyl perbenzoate as polymerisation initiators. The pH of the suspension was adjusted to between 7 and 7.5 by the addition of a little boric acid and the suspension was then purged with a stream of nitrogen and gently agitated whilst it was heated for 3½ hours at 68 °C followed by about 3 hours at 83 °C. At this point polymerisation was not complete but the polymer beads had become set in size so that an evaluation of the efficiency of the polymerisation reaction as related to the size of the polymer beads could then be made.

The polymer beads obtained were separated from the reaction mixture, washed well with water and dried. The beads were then passed through a series of sieves in order to determine their particle size distribution. This is shown in Table II below in which the percentage of the beads which pass through each size of sieve is given. The sieve sizes are given as the number of meshes per inch.

TABLE II

Experiment	Polyethylene oxide (% based on styrene)	Sodium dodecylbenzene sulphonate		Particle size of polymer beads (% passing through sieve)					
		- % by weight		Sieve size					
		Based on styrene	based on polyethylene oxide	10	22	30	44	60	Residue
A	0.3	0.03	10	14	74	8	2	1	1
B	0.3	0.045	15	65	32	1	1	0.5	0.5
C	0.45	0.045	10	1.5	86.5	8	3	0.5	0.5
D	0.45	0.045	10	1	91.5	6	1.5	—	—
E	0.45	0.06	13.3	1	54	27	11	4	2
F	0.6	0.045	7.5	1.5	93	3	2	0.5	0.5
G	0.9	0.045	5	1	95.5	2	1	0.5	0.5
H	0.9	0.06	6.7	1	96	1.5	1	0.5	0.5

A further experiment carried out under the conditions as used in Experiment A, except that the amount of sodium dodecylbenzene sulphonate used was 0.21% by weight based on the weight of styrene, that is 70% by weight based on the polyethylene oxide, gave a very satisfactory polymerisation which was conducted throughout as a suspension polymerisation process.

Two comparative experiments were also carried out using 0.3% and 0.6% by weight based on the styrene of the polyethylene oxide and in which no surface active agent was used. In these two instances less satisfactory results were obtained from the polymerisation reaction in that the beads showed a tendency to agglomeration thereby preventing the reaction from being carried to completion; this agglomeration which occurred also prevented the carrying out of a sieve analysis on the polymer beads.

Thus this Example illustrates that a suspension polymerisation process is advantageously carried out using a high molecular weight polyethylene oxide in conjunction with a small amount of an anionic surface active agent as suspension stabiliser. This Example also illustrates that a narrower distribution of polymer bead size is obtained when the amount of the polyethylene oxide is increased keeping the amount of surface-active agent constant at a low figure.

EXAMPLE 12

This Example again illustrates a successful bead polymerisation process for the production of a high impact polystyrene

material using a high molecular weight polyethylene oxide as suspension stabiliser in the presence of a minor amount of an anionic surface-active agent. The Example also illustrates the effect on the particle size distribution of the polymer beads which is produced by the addition of a small amount of water-soluble inorganic metal halide.

Six exemplifying experiments (J to O) were each carried out as follows:

A sample of pre-polymer polymerised to about 15% conversion was prepared by the mass polymerisation of 100 parts of styrene in the presence of 6 parts of a GR-S rubber as described in Example 9. This pre-polymer was then suspended in water and polymerised by a bead polymerisation process as described in Example 11; the amount of the polyethylene oxide and sodium dodecylbenzene sulphonate used in each experiment being that given in Table III below. However, to each aqueous suspension there was also added before commencement of the polymerisation a small quantity of potassium chloride (except in run O where sodium chloride was used instead). The amount of such addition used in each experiment is given in Table III below as a percentage by weight based on the quantity of water present in the system. In each experiment the polymerisation process proceeded smoothly and the polymer beads were obtained and sieved as in Example 11 to determine their particle size distribution, which is given for each experiment in Table III.

TABLE III

75	Experiment	Poly-ethylene oxide (% based on styrene)	Sodium dodecyl-benzene sulphonate		KCl (% based on water)	Particle size of polymer beads (% passing through sieve)					
			% by weight			Sieve size					
			based on styrene	based on poly-ethylene oxide		10	22	30	44	60	Residue
85	J	0.45	0.045	10	0.25	2	17	11	24	26	11
	K	0.45	0.045	10	0.5	1	13	10	10	19	46
	L	0.6	0.045	7.5	0.5	1	11	9	38	27	10
	M	0.6	0.045	7.5	1.0	2	24	8	14	27	21
	N	0.6	0.06	10	0.5	1.5	22	28	29.5	12.5	6.5
	O	0.6	0.045	7.5	0.4*	1	13.5	9.5	15.5	32	36

* NaCl used in place of KCl

Comparison of the particle size distribution of the polymer beads obtained by the experiments of this Example with that obtained from the experiments of Example 11, particularly the comparison of experiments D, J and K and of experiments F, L and M, show that the addition of a small amount of potassium chloride to the reaction medium results in polymer beads of much smaller size being obtained though at the expense of some loss of the narrowness of the polymer size distribution. In all the experiments the polymerisation process proceeded smoothly as a bead process and there was no tendency for the polymer beads to agglomerate. The results of Experiment O shows that the potassium chloride can equally well be replaced by sodium chloride.

WHAT WE CLAIM IS:—

1. A process for the polymerisation of a normally water-insoluble ethylenically unsaturated organic compound capable of radical addition polymerisation by a suspension polymerisation process, which process comprises polymerising the organic compound in aqueous suspension in the presence as suspension stabiliser of a minor amount of a polyalkylene oxide compound having a molecular weight of at least 20,000.
2. A process as claimed in claim 1, in which the polyalkylene oxide compound used has the formula $XO(R'O)_nX$ where each X represents a hydrogen atom or an alkyl group, each R' represents a divalent aliphatic group having 2 to 4 carbon atoms or an α -phenylethylene group, and n is an integer sufficiently large to give the polyalkylene oxide compound a molecular weight of at least 20,000.
3. A process as claimed in claim 2, in which the polyalkylene oxide compound is a polyalkylene ether glycol having a molecular weight of 200,000 to 3,000,000.
4. A process as claimed in claim 3, in which the polyalkylene ether glycol is a polyethylene oxide.
5. A process as claimed in either of claims 3 or 4, in which the polyalkylene ether glycol has a molecular weight of the order of 400,000.
6. A process as claimed in any one of the preceding claims, in which the polyalkylene oxide compound is used as suspension stabiliser in an amount of from 0.1 to 5% by weight based on the weight of the ethylenically unsaturated organic compound or compounds.
7. A process as claimed in claim 6, in which the amount of polyalkylene oxide compound used is from 0.3 to 1% by weight based on the weight of the ethylenically unsaturated organic compound or compounds.
8. A process as claimed in any one of the preceding claims, in which there is also present a surface-active agent in an amount

which is insufficient to cause an emulsion polymerisation process to result.

9. A process as claimed in claim 8 in which the surface-active agent is a cationic surface-active agent.

10. A process as claimed in claim 8, in which the surface-active agent is an anionic surface-active agent.

11. A process as claimed in claim 10, in which the anionic surface-active agent is an alkali metal salt of an alkylaryl sulphonate acid or an alkyl-sulphuric or -sulphonic acid.

12. A process as claimed in claim 11, in which the anionic surface-active agent comprises sodium dodecylbenzene sulphonate.

13. A process as claimed in any one of claims 8 to 12, in which the surface-active agent is present in an amount of from 5 to 15% by weight based on the weight of the polyalkylene oxide compound.

14. A process as claimed in claim 13, in which the said amount is between 8 and 12%.

15. A process as claimed in any one of the preceding claims, in which there is also present in the reaction medium a water-soluble metal or ammonium halide in an amount not greater than 5% by weight based on the weight of water present.

16. A process as claimed in claim 15, in which the said halide is a chloride.

17. A process as claimed in claim 16, in which the said halide is potassium or sodium chloride.

18. A process as claimed in any one of claims 15 to 17, in which the said halide is present in an amount not greater than 1% by weight based on the weight of water present.

19. A process as claimed in claim 18, in which the amount of the said halide is between 0.4 and 0.7% by weight based on the weight of water present.

20. A process as claimed in any one of the preceding claims, in which vinyl chloride is polymerised.

21. A process as claimed in any one of claims 1 to 19, in which there is polymerised a lower alkyl ester of acrylic or methacrylic acid.

22. A process as claimed in any one of claims 1 to 19, in which there is polymerised a vinyl-aromatic compound.

23. A process as claimed in claim 22, in which styrene is polymerised.

24. A process as claimed in any one of the preceding claims, in which the ethylenically unsaturated organic compound is polymerised in the presence of a preformed polymer as well as the polyalkylene oxide compound present as suspension stabiliser.

25. A process as claimed in claim 24, in which the preformed polymer is a sulphur-vulcanisable natural or synthetic rubber.

26. A process as claimed in claim 25, in which the hydrocarbon rubber is a butadiene-styrene copolymer which has been prepared from 60 to 90% by weight of butadiene and 40% to 10% of styrene.

27. A process as claimed in any one of claims 24 to 26, in which the preformed polymer is present in an amount of from 3 to 40% by weight based on the weight of the ethylenically unsaturated organic compound.

28. A process as claimed in claim 27, in which the preformed polymer is present in an amount of from 5 to 10% by weight based on the weight of the ethylenically unsaturated organic compound.

29. A process as claimed in any one of the preceding claims, in which the ethylenically unsaturated organic compound is first subjected to a mass pre-polymerisation treatment and the resulting pre-polymerised mass suspended in an aqueous medium using the polyalkylene oxide compound as suspension stabiliser before completion of the polymerisation as a suspension process.

30. A process according to any one of the preceding claims, in which there is

initially present in the aqueous suspension a radical-addition polymerisation initiator.

31. A process according to any one of the preceding claims, in which the aqueous suspension is maintained between pH 7 and 11 during the polymerisation reaction.

32. A process according to claim 31, in which the aqueous suspension is maintained between pH 9 and 11 during the polymerisation reaction.

33. A process for the polymerisation of an ethylenically unsaturated organic compound conducted substantially as hereinbefore described with particular reference to any one of the Examples.

34. A polymerised ethylenically unsaturated organic compound whenever prepared by a process as claimed in any one of the preceding claims.

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PROVISIONAL SPECIFICATION

Suspension Polymerisation Process

We, "SHELL" RESEARCH LIMITED, a British company, of St. Helen's Court, Great St. Helen's, London, E.C.3., do hereby declare this invention to be described in the following statement:—

This invention relates to a process for the polymerisation of an ethylenically unsaturated organic compound which is conducted in an aqueous suspension.

The radical-addition polymerisation of an ethylenically unsaturated organic compound is often conducted in a suspension or dispersion of the monomer in water. The resulting polymer is produced in the form of beads, that is as small particles of solid polymer, which are suspended in the aqueous dispersion, such processes are therefore sometimes termed "bead", suspension or dispersion polymerisations. When such a polymerisation process is complete the polymer obtained may be readily separated from the dispersion by filtering or centrifuging the formed polymer beads from the aqueous medium and these beads are then readily purified by a simple washing procedure. If desired, the polymer particles may subsequently be further purified by an extrusion process in which the polymer is melted, forced through an extrusion die-head where it solidifies and then out into small polymer particles called "nibs" which are very suitably used in moulding procedures and similar processing techniques.

The advantages of a suspension polymerisation process over one conducted in an emulsion or as a mass polymerisation process are that the formed polymer particles obtained thereby are in a solid form which are of high purity and can be readily separated from the reaction mixture and processed. Moreover in such a process the temperature is readily controlled and heat transfer problems are minimized. On the other hand an emulsion polymerisation has the disadvantage that a polymer latex is obtained which must first be coagulated to give a solid polymer before this can be separated from the surrounding medium, and a mass polymerisation process has the disadvantage that the resulting polymer is often found to contain an appreciable quantity of occluded monomer, which is only completely separated from the polymer with difficulty.

The disadvantage of operating a suspension polymerisation process is the difficulty of maintaining a satisfactory dispersion of the monomer or reaction medium in the aqueous medium, that is preventing the agglomeration of the dispersed polymer beads formed during the polymerisation reaction, and of obtaining such beads in a suitable size. Although the monomer can be kept suspended in the aqueous medium by vigorous stirring or otherwise agitating the reaction mixture, this method does not

give a stable suspension and it is necessary to use a suitable suspension stabiliser. Often this is a finely-divided solid which, when added to the reaction mixture, gives a stable suspension from which the solid does not settle out even if the mixture is only being stirred at a slow rate.

Various inorganic substances have been proposed as suspension stabilisers for use in the bead polymerisation of ethylenically unsaturated organic compounds. These include, for example, talc, clay, barium sulphate and calcium phosphate and oxalate. Water-soluble organic stabilisers have also been used in such polymerisations. For instance, polyvinyl alcohol has been found to give quite good results when used in a process for the suspension polymerisation of certain monomers, for example styrene; gelatine, fish-glue, pectin and salts of polyacrylic acids and styrene-maleic anhydride copolymers have also been proposed for this purpose but the use of starch and gelatine as suspension stabilisers for the polymerisation of a solution of 6% by weight of a rubbery butadiene-styrene copolymer in monomeric styrene has been found to give poor results.

Therefore, as illustrated above in two particular examples, the suspension stabilisers of the prior art do not always give satisfactory results either in that the suspension obtained is not stable throughout the entire course of the polymerisation, or that polymer beads of an inconveniently small size are sometimes obtained. For the latter purpose it is desirable to obtain beads which are as large as possible, but which are of comparable purity to those of smaller size, as the larger the beads the easier is their separation from the reaction mixture. There is a great variety of monomers which can be polymerised in a suspension process and the conditions for the polymerisation of each of such monomers vary to a great extent so that a suspension stabiliser which is eminently satisfactory for the polymerisation of one monomer under certain conditions may be quite unsuitable for polymerising the same or a different monomer under different conditions or a different monomer under the same conditions. It has therefore been a matter for considerable research to find alternative suspension stabilisers to those of the prior art, which alternative stabilisers in special circumstances yield results which are comparable to or better than those obtained using the conventional stabilisers, for example those previously mentioned.

It has now been discovered that the polymerisation of an ethylenically unsaturated organic compound can be very suitably conducted in an aqueous suspension which is stabilised by the presence of a polyoxyalkylene oxide compound of high molecular

weight. Such a polymerisation process proceeds smoothly and is readily amenable to good temperature control. Furthermore the polymers are often produced in a high state of purity and in beads of a very convenient size which may be quite substantial. Such a use for polyalkylene oxide compounds is quite distinct from the well-known use of low molecular weight polyalkylene ether glycols and their derivatives as non-ionic emulsifying agents in polymerisation processes carried out in emulsion as distinct from suspension or bead polymerisation processes.

Accordingly, the process of the invention is one for the suspension polymerisation of an ethylenically unsaturated organic compound which comprises polymerising the organic compound in aqueous suspension in the presence as suspension stabiliser of a minor amount of a polyalkylene oxide compound as hereinafter defined having a molecular weight of at least 20,000.

The polyalkylene oxide compound for use in the process of the present invention is hereby defined as one that has been derived by polymerisation of an alkylene oxide or copolymerisation of a mixture of alkylene oxides. The term polyalkylene oxide compound is herein intended to extend not only to polyalkylene ether glycols but also to ethers and esters of such glycols. Thus normally the polyalkylene oxide compound used will be one of the general formula



where each X represents hydrogen or an alkyl, aryl, acyl or aroyl group, each R represents a divalent aliphatic or substituted aliphatic group other than a methylene or substituted methylene group and n is an integer sufficiently large to give the polyalkylene oxide compound a molecular weight of at least 20,000 (compounds of the above formula except that R is a methylene or substituted methylene group are more correctly designated as polyaldehydes or derivatives of polyformaldehyde and, as such, their use is outside the scope of the present invention). Furthermore, if desired, the polyalkylene oxide compound may be one which has been derived from a polyhydroxy-nucleating agent by condensation of its hydroxyl groups with an alkylene oxide to produce a polyalkylene oxide compound of the desired molecular weight; for instance a condensation product of the formula $HO(CH_2CH_2O)_n.C_6H_4.(OCH_2CH_2)_mOH$ which is derived from ethylene oxide and a dihydroxy benzene such as hydroquinone or resorcinol. It is of course possible to use as such a polyhydroxy nucleating agent a trihydroxy compound such as glycerol, pyrogallol, or a tetrahydroxy compound such as durene or pentaerythritol.

Preferred polyalkylene oxide compounds

for use in the present invention are those derived from the homo- or co-polymerisation of styrene oxide and lower alkylene oxides such as ethylene oxide; 1,2-propylene oxide; 1,3-propylene oxide; tetrahydrofuran; and 1,2-butylene oxide; that is compounds of the general formula $XO(R'O)_nX$ where each X represents a hydrogen atom or an alkyl, aryl, acyl or aroyl group, each R' represents a divalent aliphatic group having 2 to 4 carbon atoms or an α -phenylethylene group and n is an integer sufficiently large to give the polyalkylene oxide compound a molecular weight of at least 20,000. The self- or inter-polymers of ethylene oxide and 1,2-propylene oxide are particularly useful in the process of the invention.

The polyalkylene oxide compounds for use in the present process have a minimum molecular weight of 20,000 and, as previously explained, they may be polymeric glycols or mono- or di-ethers or esters thereof. However, the preferred compounds are polyalkylene oxides, that is polyalkylene ether glycols, having a molecular weight of 200,000 to 3,000,000. Polyalkylene oxides, and particularly polyethylene oxides, having a molecular weight of the order of 400,000 are especially suitable for the present process. The limitation of the invention to the use of polyalkylene oxides having a molecular weight greater than 20,000 is an approximate one as the exact determination of the molecular weight of any particular sample of a polyalkylene oxide is not readily made. Furthermore any such molecular weight determination gives an average value which may vary to a small degree depending upon the molecular weight determination method used. However, the high molecular weight polyalkylene oxides used in the present invention constitute a readily recognisable class of compounds quite distinguishable from the polyalkylene oxide compounds, hitherto commercially available, that have molecular weights of the order of not more than a few thousand. The molecular weight of such low molecular weight compounds is readily determined from measurements of their hydroxyl number, but the high molecular weight polyalkylene oxides have too low a hydroxyl number to enable an accurate determination of their molecular weight to be made by this method.

The molecular weight of the polyalkylene oxide used in the present invention may be determined by any of the conventional methods used for determination of the molecular weights of polymeric materials, for example by osmometry or by viscometry. The molecular weight of a sample of a polyethylene oxide is readily determinable by measurement of the intrinsic viscosity at 35°C of a 0.1% solution of the compound in water and using the following conver-

sion factor given in the Journal of Applied Polymer Science, Volume I, no. 1, page 60, namely:

$$IV = 6.4 \times 10^{-5} M^{0.82}$$

where I.V. is the intrinsic viscosity of the polyethylene oxide at 35°C and M is its average molecular weight; the molecular weights of the various polyethylene oxides used in the following Examples have been determined by this method and by making use of the above relation between intrinsic viscosity and molecular weight.

Polyalkylene oxides of molecular weight above 20,000 may be prepared from the monomeric compounds in several different ways. For instance, alkylene oxides may be polymerised to produce these high molecular weight polymers in the presence of catalysts of various types, which include, among others, alkoxides and aroxides of metals from Groups 2 to 5 of the Periodic Table of elements; metal alkyls and metal alkyl halides derived from metals of Group 2 and 3 of the Periodic Table and Friedel-Crafts catalyst complexes such as complexes of the alkylene oxide with ferric or stannic chloride. It has also been proposed to use as catalysts for the polymerisation of alkylene oxides certain synergistic combinations of the catalysts described above. The mono- or di-ethers and esters of the polyalkylene oxides may be prepared from the polyalkylene oxides themselves, that is the polyalkylene ether glycols, in the conventional manner.

The polyalkylene oxide compounds which find use in the present invention are solid materials which have only a limited solubility in water. It is believed that a slight solubility of the polyalkylene oxide compound in water is desirable and accordingly a polyethylene oxide is the preferred suspension stabiliser of the invention, as such a compound has a greater solubility in water than a polypropylene or higher oxide, though in any case the solubility of a polyalkylene oxide in water is quite small.

The amount of polyalkylene oxide compound required to give a stable dispersion of the monomer in water depends upon the nature of the monomer and the conditions to which the dispersion is to be subjected. It is of course desirable to use the minimum amount of polyalkylene oxide compound necessary to give a stable suspension of the monomer in the aqueous medium as there is then less risk of contamination of the formed polymer by the excess suspending agent, that is the polyalkylene oxide compound, and polymer beads of larger size are also more likely to be obtained. An amount of polyalkylene oxide compound between 0.1 and 5% and particularly between 0.3 and 1% by weight based on the monomer has been found to be particularly suitable

for the purposes of the invention. However, the optimum amount of polyalkylene oxide is in some ways dependent on its molecular weight and if this is not of the preferred order, it may be necessary to use a slightly higher proportion of the polyalkylene oxide. The minimum amount of polyalkylene oxide which gives completely satisfactory dispersion of the monomer or monomers in the aqueous medium throughout the course of the polymerisation and at the same time results in the ready production of suitably pure beads of large size can readily be found from the results of a few small scale tests. In most cases an amount of about 0.5% by weight of the monomer will be found to be eminently suitable, though in particularly favourable cases an amount of 0.3% may well suffice.

The monomer to be polymerised is one which is insoluble in water and capable of radical-addition polymerisation by a suspension polymerisation process. Thus the process of the invention finds particular application in the suspension polymerisation of styrene and vinyl chloride. However, the process may also be used to polymerise vinyl-aromatic compounds in general, that is to polymerise, for example, vinyl toluene, divinyl benzene, α -methyl styrene and nuclear halogenated styrenes, as well as mixtures of one or more of such vinyl aromatic compounds including styrene with one or more conjugated dienes such as butadiene, isoprene, chloroprene, 2,3-dimethyl-butadiene and piperylene to form resinous copolymers. Ethylenically unsaturated organic compounds which are not hydrocarbons may also be polymerised by the process of the invention. Thus, for instance, besides vinyl chloride, which is particularly suitably polymerised by the present process, there may be polymerised vinylidene chloride, methyl methacrylate, ethyl acrylate and acrylonitrile. Mixtures of two or more ethylenically unsaturated organic compounds may of course be copolymerised and the process of the invention is particularly suited to the production of graft copolymers by the polymerisation of one or more monomers in the presence of a preformed polymer of copolymer. For instance, there may be produced by the process of the invention a modified or toughened polystyrene having a high impact strength by polymerising styrene in the presence of a preformed rubbery polymer such as, for example, polybutadiene, polyisoprene, a rubbery styrene-butadiene or acrylonitrile-butadiene copolymer or in the presence of a natural rubber material. Such preformed polymers can of course have been previously prepared by any suitable polymerisation process and, if desired, the preformed polymers can comprise the stereospecific polydienes such as cis-1,4-isoprene

or cis- or trans-1,4-polybutadiene or the elastomeric ethylene-propylene copolymers.

If desired, the monomer or monomers to be polymerised can be subjected to a pre-polymerisation step carried out as a mass polymerisation and then the partially polymerised pre-polymer produced is suspended in an aqueous medium using one of the specified polyalkylene oxide compounds as the suspension stabiliser and the polymerisation completed by the process of the invention. If desired, in such a process a further quantity of monomer can be added to the dispersion during the polymerisation process. For instance a modified polystyrene material of high impact strength may be very advantageously obtained by subjecting a solution of a rubbery styrene-butadiene copolymer in monomeric styrene to a pre-polymerisation stage by heating the mixture in the absence of water, if necessary in the presence of a peroxide initiator, until approximately 15% by weight of the monomeric styrene has polymerised. The mixture is then dispersed in approximately an equal volume of water, the polyalkylene oxide added as suspension stabiliser and the dispersion then agitated and subjected to polymerising conditions. There are obtained beads of a high-impact polystyrene which are readily separated by centrifuging the reaction mixture.

In the preferred embodiment of the invention, as outlined immediately above, there may conveniently be used a pre-polymerisation stage which is sufficient to polymerise from 5 to 40% and particularly from 10 to 20% by weight of the monomer. Such a pre-polymerisation stage is carried out in the absence of water, but there may be present conventional additives such as radical-addition polymerisation initiators; for example, peroxy compounds such as benzoyl or lauryl peroxide, tert-butyl perbenzoate, cumyl hydroperoxide, or azo compounds such as azo-bis-isobutyronitrile or azo-bis-cyclohexane carbonitrile; chain transfer agents, for example tert.-dodecyl mercaptan; lubricants such as butyl stearate and glycerol mono-stearate, and other additives such as, for example, antioxidants and fillers. The pre-polymerisation stage can, if desired, be carried out in the absence of a radical-addition initiator, the polymerisation being initiated by ionizing radiation, ultra-violet light or simply by heating the reaction mixture to a suitable temperature.

When the preferred embodiment of the invention is used to prepare a high impact polystyrene it is convenient to dissolve a proportion, usually between 3 and 40% and particularly between 5 and 10%, of a rubbery polymer in the monomeric styrene, to subject this solution to a pre-polymerisation step and then to disperse the pre-polymerised

mass in water with the aid of the polyalkylene oxide suspension stabiliser before completing the polymerisation reaction as a suspension process. The rubber is very suitably a styrene-butadiene copolymer of the GR-S type, that is one prepared from 60-90% by weight of butadiene and 40 to 10% of styrene, though there may also be used rubbery butadiene-acrylonitrile copolymers, polybutadiene, polyisoprene or natural rubber, as well as stereospecific polymers such as cis-1,4-polyisoprene, cis- or trans-1,4-polybutadiene or an elastomeric ethylene-propylene copolymer. If necessary the rubber may contain a small amount of an antioxidant or other antidegradant.

When a pre-polymerisation stage is used, the mass polymerisation is interrupted after a suitable polymerisation time and the partially polymerised mass then dispersed in an aqueous medium. This is usually water, but if desired it can be an aqueous solution of a suitable salt. Normally it is desirable to disperse the pre-polymerised mass in the ratio of 1 part of pre-polymer to between 0.5 and 5 parts by volume of water, though smaller or larger ratios can be used; particularly good results are achieved when the pre-polymerised mass is dispersed in approximately an equal volume of water. When no pre-polymerisation stage is used it will be found very suitable to disperse the monomer in from 1 to 5 parts by weight of water. Thus when vinyl chloride is polymerised by the process of the invention it is very convenient to disperse the monomer in about 2.5 parts by weight of water.

The suspension process of the invention is normally carried out in the presence of a radical-addition polymerisation initiator such as an organic peroxide or hydroperoxide or an aliphatic or cyclo-aliphatic azo compound. It is usual to stir the reaction mixture during the polymerisation process, which is preferably conducted in an inert atmosphere, for example under nitrogen or hydrogen, in order to avoid the deleterious effects which may result when radical-addition polymerisations are conducted in the presence of air or oxygen. It is therefore desirable to purge the suspension before subjecting it to polymerising conditions with a stream of an inert gas, such as nitrogen. If desired, there may be incorporated in the suspension other materials such as chain-transfer agents, for example, tert-dodecyl mercaptan, lubricants such as, for example, stearic acid or butyl stearate and antioxidants such as, for example, 2-tert-butyl-4-methyl phenol, styreneated resorcinol, trio(nonyl-phenyl) phosphite and N-substituted phenylene diamines.

The process of the invention may be conducted at the usual temperature for suspension polymerisation processes. Often this

will be between 50°C and 100°C, though higher or lower temperatures can be employed where necessary. When temperatures which are in excess of the boiling point of the monomer are employed it will be necessary to conduct the polymerisation in a pressurized reactor to prevent loss of the monomer by evaporation. It is then highly desirable to pressurize the reactor with an inert gas such as nitrogen in order to prevent the polymerisation reaction from being to be affected by the presence of oxygen in the reaction system. Alternatively, the monomer may be suitably polymerised in a closed reactor under autogenic pressure at a suitable temperature, for example, vinyl chloride may be so polymerised at a temperature of approximately 50°C, and styrene at a temperature up to about 130°C, though in this case it is usual to commence the polymerisation at a temperature below 100°C and raise it to a figure above 100°C only in the later stages of the reaction.

The aqueous suspension in which the process of the invention is conducted should, preferably, have a controlled pH as variations in the acidity and alkalinity of the reaction mixture often have a considerable effect on the rate of polymerisation and the effectiveness of the suspension stabiliser. Furthermore, it is found that the polyalkylene oxide compound used as suspension stabiliser tends to be unstable in an acidic medium. Thus it is desirable that the reaction mixture should be maintained within a pH of 7 to 11 and more preferably within the pH range of 9 to 11. It is particularly found that control of pH becomes more important as the amount of polyalkylene oxide compound is decreased and, if desired, control of pH may in many cases be obviated by the use of larger quantities of the stabiliser, though if possible an excess of the polyalkylene oxide compound is desirably avoided, as previously explained. The alkalinity of the reaction mixture can be suitably maintained by the addition of a buffer compound; for example small quantities of sodium borate or sodium acetate or even sodium hydroxide can be added to the reaction mixture and the pH of the mixture thereby controlled and maintained at a convenient value.

The polyoxyalkylene compounds used in the process of the invention can, of course, be used in combination with the suspension stabilisers of the prior art. In addition, it may sometimes be found desirable to use the polyoxyalkylene compound in conjunction with a minor proportion, based on the polyoxyalkylene compound of a surface-active agent, for example an alkali metal soap or an alkali metal salt of an alkylaryl sulphonate.

The suspension process of the invention

results in the production of polymer beads. The beads produced by the invention are often of quite a large size and bead diameters of 0.05 to 0.07 inches are frequently obtained. The polymer beads are conveniently separated from the reaction mixture by filtration or by centrifuging the mixture and the separated beads are then washed well with water and dried. If desired, the polymer beads may be further purified by an extrusion process, the extruded material being chopped into small particles termed "nibs" which are very suitably used in conventional moulding and fabricating procedures.

The invention will now be illustrated by the following Examples.

EXAMPLE 1

In 100 parts by weight of monomeric styrene, which had been distilled in order to remove any dissolved polymerisation inhibitor, there was dissolved 6 parts by weight of a GR-S rubber crumb which had been prepared by the copolymerisation of 76.5% by weight of butadiene and 23.5% by weight of styrene at a temperature of about 50°C and which contained about 1 part by weight of trio-(nonyl-phenyl) phosphite as rubber antioxidant. To this solution there was also added 3.5 parts by weight of butyl stearate as lubricant and the mixture was then purged with nitrogen to remove oxygen from the solution and thereafter pre-polymerised with stirring to a polymer conversion of monomeric styrene of about 15% by heating the mixture in bulk in the absence of a radical-addition polymerisation initiator to a temperature of 105°C for 4.75 hours.

The pre-polymerised mass was suspended in 150 parts by weight of water and the resulting suspension stabilised by the addition of 0.5% by weight of a polyethylene oxide having a molecular weight of approximately 400,000. To the mixture there was added 2 parts by weight of azo-bis-cyclohexane carbonitrile as radical-addition polymerisation initiator. The suspension was then purged with a stream of nitrogen and gently agitated whilst it was subjected to the following polymerisation cycle:

7 hours at 90.°C

1 hour at 100 °C

13 hours at 120 °C

Initially the polymerisation was conducted at atmospheric pressure but during the cycle it became necessary to conduct the reaction in a closed reactor under autogeneous pressure to prevent evaporation of monomer and water. At the end of the cycle it was found that a polymerisation conversion of 99.8% had occurred. The polymer beads obtained were separated from the reaction mixture, washed well with water and dried to yield a polystyrene having an impact

strength of 1.04 foot pounds per Izod notch.

EXAMPLE 2

A solution of 6 parts by weight of the GR-S rubber in 100 parts by weight of monomeric styrene containing 3.5 parts by weight of butyl stearate was prepared as described in Example 1. This mixture was purged with nitrogen and then subjected to a bulk pre-polymerisation stage by heating it with stirring for 10 hours at 95°C in the absence of a radical-addition polymerisation initiator; at the end of this time it was shown that approximately 15% by weight of the styrene had polymerised.

The pre-polymerised mass was suspended in 150 parts by weight of water containing 1 part by weight of a polyethylene oxide of molecular weight about 400,000 and the resulting dispersion purged with a stream of nitrogen and vigorously agitated. Polymerisation of the styrene was effected by adding to the mixture 0.2% by weight based on the styrene of benzoyl peroxide as polymerisation initiator and then subjecting the reaction mixture to a temperature of 92°C for 24 hours, after which the polymer beads obtained were separated from the reaction mixture, washed well with water and dried. The polystyrene beads were found to be of a fairly large size having a diameter of 0.05 to 0.07 inches and were of high purity.

EXAMPLE 3

The process of Example 1 was repeated but using a 0.3 part by weight of the polyethylene oxide as suspension stabiliser. The polymerisation process proceeded perfectly satisfactorily. The polystyrene beads obtained were of a conveniently large size and moreover were readily separated from the reaction mixture and purified.

EXAMPLE 4

Monomeric styrene which had been distilled to remove any polymerisation inhibitor was suspended in 5 times its volume of water using 1% by weight based on the styrene of a polyethylene oxide having a molecular weight of 1,800,000 as suspension stabiliser. There was then added to the suspension 0.2% by weight based on the styrene of benzoyl peroxide as polymerisation initiator and the polymerisation was conducted at 92°C for 20 hours; the mixture being vigorously agitated throughout. After 2.5 hours of the polymerisation a further 0.2% of benzoyl peroxide was added to the reaction mixture. The polymerisation reaction proceeded smoothly throughout and polystyrene beads of good quality were obtained.

EXAMPLE 5

The procedure used to prepare the pre-polymer of Example 2 was repeated. The pre-polymerised mass was then dispersed in 5 times its own volume of water using 1% by weight based on the styrene of a polyethylene oxide of M.W. 400,000 as suspen-

sion stabiliser. To the suspension of monomer in water there was added 0.1% by weight based on the styrene of azo-bis-isobutyronitrile as polymerisation initiator and the polymerisation reaction was conducted at 92°C for 10 hours; a further 0.1% of the initiator being added after 3 hours.

The polymerisation process proceeded smoothly and beads of a high impact polystyrene were obtained which were of good quality.

EXAMPLE 6

The procedure of Example 5 was repeated except that the mass pre-polymerisation stage was continued until 17.3% conversion had occurred and except that the initiators used were 0.2% by weight based on the styrene of tert-butyl perbenzoate added to the initial suspension of the pre-polymer and 0.2% by weight based on the styrene of benzoyl peroxide which was added after a further 3 hours.

The polymerisation proceeded smoothly and high impact polystyrene beads of good quality were obtained.

EXAMPLE 7

This Example illustrates the production of a high impact polystyrene on a larger scale than that used in the previous Examples.

A solution of 6% by weight of the GR-S rubber used in Example 1 was prepared in 0.4 gallons of monomeric styrene which had been distilled to remove polymerisation inhibitor. The solution was purged with nitrogen to remove oxygen, agitated and heated for 6 hours under autogeneous pressure at 100°C. The conversion in their mass pre-polymerisation stage was shown to be about 15%.

The pre-polymer and residual monomer were then dispersed in 0.6 gallon of water using 0.3% by weight based on the styrene of a polyethylene oxide of molecular weight 400,000. The pH of the suspension was adjusted to pH 10 to 11 by the addition of a small quantity of aqueous sodium hydroxide solution. The dispersion was agitated and 0.2% by weight based on the styrene of azo-bis-cyclohexane carbonitrile and 0.05% by weight based on the styrene of tert-butyl perbenzoate were added as polymerisation initiators. Agitation of the dispersion was continued while it was subjected to the following polymerisation cycle:—

2 hours at 68°C
2 hours at 83°C
2 hours at 115°C
2 hours at 130°C

At the end of this cycle the formed polymer beads were separated from the reaction mixture and were found to be well-formed and of comparatively large size. The impact strength of the material as shown to be 1.06 foot pound per Izod notch.

EXAMPLE 8

The procedure of Example 7 was repeated on a larger scale using 20 gallons of monomeric styrene and 30 gallons of water as dispersing medium for the pre-polymer obtained therefrom. There were formed at the end of the polymerisation cycle beads of similar good size and appearance as those which were produced in Example 7.

This Example illustrates the relationship between the molecular weight of the polyethylene oxide used as suspension stabiliser and the amount of it required to give the most satisfactory results in the production of beads of high impact polystyrene.

A solution in distilled monomeric styrene was prepared containing 3.5% by weight of butyl stearate as lubricant and 6% of a GR-S rubber which had been produced by copolymerisation of 76.5% by weight of butadiene and 23.5% by weight of styrene at a temperature of about 50°C and which contained about 1% by weight of tri-(nonyl-phenyl)phosphite as antioxidant. The solution was purged with nitrogen to remove oxygen from the solution and thereafter polymerised with stirring to a polymer conversion of monomeric styrene of approximately 15% by heating the mixture in bulk in the absence of a polymerisation initiator to a temperature of 100°C for 6 hours.

Samples of the pre-polymer were dispersed in 1.5 times their volume of water using a polyethylene oxide, of a molecular weight and in a percentage by weight based on the weight of styrene as stated in the Table given below. In each case the dispersion was buffered at pH 9 by the addition of a boric acid/sodium hydroxide/potassium chloride aqueous solution as buffer and 0.2% by weight of benzoyl peroxide was added as polymerisation initiator. Each reaction mixture was then heated at 92°C for approximately 20 hours.

The following Table describes the results of the polymerisation reaction and the nature of the polymer beads obtained.

TABLE			Result
Molecular weight	Amount used	%	
5	400,000	0.3	Dispersion satisfactory, good beads obtained.
	400,000	0.2	Dispersion satisfactory, fairly good beads obtained.
10	100,000	0.15	Initial dispersion satisfactory, giving beads of fair quality, but dispersion not maintained throughout the polymerisation.
15	100,000	0.4	Initial dispersion and polymerisation satisfactory, but dispersion not maintained towards the completion of the polymerisation.
20	100,000	1.0	Dispersion satisfactory and beads of suitable size obtained, but difficulty experienced in maintaining complete dispersion towards the completion of the polymerisation.
25			Dispersion satisfactorily maintained throughout the polymerisation. Beads of good size and appearance obtained.
30	100,000	2.5	Dispersion obtained but this had a tendency to froth and form an aqueous emulsion of the monomer. Polymerisation satisfactory, polymer beads obtained.
35	4,000,000	0.5	Initial dispersion, but polymer beads obtained were of only poor quality.
40	4,000,000	0.2	Initial dispersion difficult, poor polymer beads obtained.
45	4,000,000	0.1	

This Example illustrates that preferably the polyethylene oxide used has a molecular weight in the region of 400,000 and that the quantity of the suspension stabiliser required to achieve a completely satisfactory process with stabilisers of different molecular weights increases as the molecular weight varies from the preferred value of about 400,000.

EXAMPLE 10

This Example illustrates the suspension polymerisation of methyl methacrylate using a polyethylene oxide of high molecular weight as suspension stabiliser.

A dispersion of 80 grams of methyl methacrylate in 320 cc. of water was prepared using 1% of a polyethylene oxide of molecular weight approximately 400,000 as suspension stabiliser. There was also incorporated into the dispersion 0.2% by weight based on the methyl methacrylate of benzoyl peroxide as polymerisation initiator and the dispersion was purged with nitrogen to remove dissolved oxygen and heated under autogeneous pressure at 85°C for 3.5 hours.

The polymerisation proceeded smoothly and beads of small size were obtained indicating that a smaller amount of the polyethylene oxide could probably have been used with advantage. However, the beads obtained were of good quality, and were readily separated from the reaction medium, washed and dried. The dried beads were compression moulded to give a disc of great clarity, thereby indicating that the beads obtained were of a satisfactory purity.

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